Catalysis Science & Technology

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Catalytic CO_2 conversion to organic carbonates with alcohols in combination with dehydration system

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Abstract

Recent progress on direct organic carbonate synthesis from CO_2 and alcohols has been reviewed on the basis of dehydration systems. Versatile dehydration systems have been developed, which drastically improves yields of the target carbonates. In this review, the feature and effect of the dehydration systems are discussed by categorizing the dehydration systems into two types, non-reactive hydration system and reactive hydration system.

1. Introduction

Conversion of CO_2 to valuable chemicals has received much attention because CO_2 is non-toxic, abundance and inexpensive C1 renewable resource.[1] However, transformation of CO_2 requires high energy input or well-designed activation system including elaborate catalysts due to its thermodynamically high stability. Recently, various methodologies have been intensively developed such as reductive transformation of CO_2 to methanol, formates and methane and non-reductive transformation to organic carbonates, carbamates, ureas, carboxylates, polyurethanes and polycarbonates.[2] Considering that the stability is attributed to the most oxidative state of CO_2, chemicals with high oxidation states will be desirable synthetic targets from the viewpoints of green chemistry and energy management. Therefore, non-reductive transformation of CO_2 is desirable to be developed and organic carbonate is one of the most promising target chemicals in terms of green sustainable chemistry for its low toxicity, non-corrosiveness and biodegradability.[3] Organic carbonates have been widely used as starting materials[4] of polycarbonate resins, polyurethane resins, electrolytes of lithium ion battery, alkylating and carbonylating reagents and inert solvents. Moreover, in the future, it is expected to be a fuel additive[5]. Among the organic carbonates, the simplest one is dimethyl carbonate (DMC), which is industrially the most important carbonate and widely studied.[6] Traditionally, DMC has been produced by phosgene method (Scheme 1 (I)).[7] This process has considerable drawbacks such as use of highly-toxic and corrosive phosgene and co-production of a large amount of inorganic salt by neutralization of HCl. Owing to these disadvantages which are far from the concept of “Green Sustainable Chemistry”, three alternative processes have been industrially developed; oxidative carbonylation of methanol by Enichem with CuCl slurry catalyst (Scheme 1 (II)),[8] two-stage process using NO and CO with $PdCl_2$+Cu/Active carbon catalyst by Ube Industries Ltd. (Scheme 1 (III)),[9] and transesterification of ethylene carbonate with methanol using anion-exchange resin by Asahi Kasei Corporation (Scheme 1 (IV)).[10] However the two processes, (II) and (III), suffer from use of toxic and hazardous CO or NO gas. On the other hand, the process (IV) is much better than the above processes from the green chemistry viewpoint that this process needs no toxic and hazardous reagents. Various effective homogeneous and heterogeneous catalysts for the process (IV) have been developed.[11] However, in general, cyclic carbonates such as ethylene carbonate or propylene carbonate need to be prepared from CO_2, CO and so on, although versatile methods for cyclic carbonate synthesis have been reported such as oxidative carbonylation of olefins with CO_2, cycloaddition of CO_2 to epoxides, oxidative carbonylation of diols and the reaction of diols with urea.[12] Ideally, direct synthesis of organic carbonates from CO_2 and the corresponding alcohols (Scheme 1 (V)) is preferable from the perspective of utilization of hazardless reagents, and low energy efficiency and cost (single reaction step). This reaction can be applied to synthesis of various linear carbonates with the corresponding alcohols. In addition, this reaction produces only water as a by-product, and alcohols including methanol, ethanol, 1-propanol, ethylene glycol, 1,2-propanediol, 1,3-propanediol and butanediol can be made from wood biomass and biomass-derived chemicals like glycerin, erythritol and sorbitol in the biorefinery,[12] which indicates that the process is expected as a green process. Recent study of life cycle analysis (LCA) also demonstrates that this process is attractive as a green sustainable process.[13] Therefore, the effective methodology for direct synthesis of organic carbonates from CO_2 and alcohols is desired to be developed. In this reaction, two crucial problems that are required to be conquered are activation of substrates (CO_2 and alcohol) and limitation of chemical equilibrium. Various effective catalysts for activation of substrates and relaxation of chemical equilibrium have been developed. Although there are excellent reviews focusing on organic carbonate synthesis with various methods,[14] there are few reviews highlighting organic carbonate synthesis from CO_2 and alcohol [14a,b,c] in spite of its being promising among various methods. In particular, dehydration systems are essential for high yield synthesis of organic carbonates. Recently, various dehydration systems have been developed and the outstanding outcomes are appearing. In this mini-review we focus on recent advances of dehydration systems for organic carbonate synthesis from CO_2 and alcohol.

2. Direct DMC synthesis from methanol and CO_2 without dehydration systems

To date, various effective homogeneous and heterogeneous catalysts for direct DMC synthesis form CO_2 and methanol have been investigated. The results are summarized in Table 1. Sn-based catalysts, CeO_2/ZrO_2 based catalysts, copper-based catalysts and etc. are well known as efficient catalysts for DMC synthesis. In terms of green chemistry, our group first in the world reported that heterogeneous catalysts of ZrO_2 or CeO_2 are effective for activation of alcohol and CO_2, and suggested that the acid-base property of CeO_2 is essential for the activity. However, without a dehydration system the yields were very low over any catalysts (< 4% based on methanol) as shown in Table 1. The biggest problem is the limitation of reaction equilibrium (Eq. 1), which blocks the reaction proceeding.

$$2CH_3OH + CO_2 \rightleftarrows (CH_3O)_2CO + H_2O \quad (1)$$

According to the previous data, the standard Gibbs energy of the reaction was estimated to be +26.2 kJ/mol,[15] which is very close to the result calculated as the real gas (+32±1 kJ/mol).[16] These results indicate that the reaction does not occur spontaneously at room temperature and the reaction is much suppressed by the reaction equilibrium. Moreover, ΔG for diethyl carbonate (DEC) was also calculated to be 35.8 kJ/mol by the same group. These results imply that the longer alkyl chain of dialkylcarbonates makes the formation of carbonates less favorable. As a result of high ΔG, the equilibrium yield of the reaction is calculated to be below 1% or 2%.[16,17] In actual, most of the reported yields by the previous works without dehydration techniques were below 2% (Table 1),[18-23] which nearly agrees with the result of the calculation method. In addition, change of the reaction conditions of temperature (323-513 K) or CO_2 pressure (<20 MPa) does not provide satisfied DMC yield,[17-23] and the calculation on the effect of the CO_2 pressure demonstrated that more than 2.41×10^4 MPa of CO_2 is required in order to progress the reaction sponteneously.[15] It should be also noted that the reaction is exothermic reaction (ΔH= -27.9 kJ mol^{-1}),[15] which suggests that lower temperature is more preferable for the reaction proceeding. Therefore, development of the dehydration systems for shifting the chemical equilibrium to the organic carbonate side is required. For the purpose, complete removal of water under the practical reaction conditions is essential for achieving the high yield of DMC.

3. Direct DMC synthesis from methanol and CO_2 with dehydration systems

Upon development of dehydration systems for organic carbonate synthesis, the most important point is that a dehydration system influences little on activation of the substrates, in that organic carbonate formation must coexist with a dehydration system under the same reaction conditions. Several dehydration systems have been developed to remove H_2O from the reaction media, and these dehydration systems can be divided into two types; non-reactive dehydration system and reactive dehydration system. These systems are summarized in Tables 2-4.

3.1 Non-reactive dehydration system

Non-reactive dehydration system means that dehydration of the reaction mixture is performed by using non-reactive compounds or special apparatus. Non-reactive dehydration system is classified into three types: gas phase system, membrane separation system and inorganic absorbent system. These systems have the advantage that fundamentally the system has little influence on the activity of catalysts and kinetics of the reaction.

3.1.1 Gas phase system

The simplest and facilest reaction system for removing water from the reaction media is gas phase reaction system, which is expected to constitute a water-free reaction system by purging with an inert gas. This system is available and convenient because no special reagent or installation is needed. Many effective catalysts such as Cu-based solid catalysts or $Co_{1.5}PW_{12}O_{40}$ in gas phase system were reported,[24] and however, the yields are below 10% and the selectivities were also below 91% (Table 2 entries 1-13). Indeed, the yields were over the equilibrium yield, indicating that the gas phase system is effective for removal of water from the reaction media.

3.1.2 Membrane separation system

The membrane separation system is promising since less energy input is needed and by-products are not formed. In addition, the regeneration procedure of the membrane is not needed, although inorganic absorbents need to be calcined or washed to remove water. Considering these aspects, the separation of H_2O using a membrane is economical. Zhong and co-workers reported that combination of polyimide-inorganic hybrid membranes and Cu catalyst in gas phase reactor showed good performance for DMC synthesis (Table 2 entry 14).[25a] The high performance is attributed to a great deal of organic functional groups such as amide and carboxyl group in the hybrid membrane, which is preferable to absorb and permeate water. The reaction system using membrane reactor provided higher conversion and selectivity (8.1-9.2% conversion and 91.4-96.0% selectivity) than the reaction system without a membrane reactor (6.5 % conversion and 90% selectivity), suggesting that this membrane separation system is effective for removal of water from the reaction media. In addition, the authors claimed that the incorporation of any types of membrane catalytic reactors hardly changed the catalytic reaction process and the reaction performances are controlled by the catalyst. However, this system has some drawbacks like limitation of CO_2 pressure (0.5 MPa) due to the air-proof conditions and permeation of the reactants. On the other hand, for the synthesis of diethyl carbonate (DEC) from ethanol and CO_2, Aresta and co-workers reported Nb_2O_5/CeO_2 catalyst combined with the pervaporation membrane of Na-A type of inorganic membrane (Table 2 entry 15).[25b] DEC was obtained in 2.3% yield by 5 times cycles of unreacted ethanol and CO_2 using the circulating reactor, which is slightly higher than the equilibrium yield. This system has the problem that high pressure of CO_2 significantly decreases the ability for separating H_2O, which needs the particular reaction system where CO_2 was depressurized after the reaction to pervaparate the liquid mixture. These two systems show that the combination of membrane is a potential method for DMC synthesis, but is far from satisfactory level at present.

3.1.3 Inorganic absorbent system

Application of inorganic absorbent is comparatively easy without a particular instrument, forms no by-products and is regenerated easily. In general, the desirable reaction temperature with inorganic dehydrating reagents is below 373 K in terms of boiling temperature of water. Srinivas and co-workers introduced molecular sieves 3A into ZrPP-HF catalyst in DMC synthesis (Table 1 entry 16).[26a] However, the DMC yield is not so high (1.7%). This is because the reaction temperature of 443 K is much higher than 373 K, which leads to failure to utilize the faculty of the molecular sieves. On the other hand, Sakakura and co-workers have reported the combination system of molecular sieves with $Bu_2Sn(OMe)_2$ catalyst using a special equipment in DMC synthesis (Table 1 entry 17).[26b,c] In order to make use of the molecular sieves effectively, this system employed a reaction process separating the reaction part (453 K) from the dehydrating part (at room temperature) and circulating a reaction mixture between these two parts (Figure 1). The DMC yield was drastically improved up to 45% in 72 h, which is much higher than that without molecular sieves. The shape and size of a molecular sieve 3A does not affect the DMC yield so much although a molecular sieve with a small size made it difficult to circulate the reaction mixture. This is the first report that DMC was produced in good yield without any by-products except water. However, the present process is not economical since it needs extra consumption of energy to heat up and cool down the reactor, and pressurize and depressurize CO_2. Recently, Segarra demonstrated that Mg-Al hydrotalcite supported silica lyogels is effective for the DMC synthesis and the DMC yield reached 15.9% at 403 K (Table 2 entry 18). According to the report, silica lyogels works as an absorbent, which shifts the equilibrium of the DMC formation reaction towards DMC side.[26d] Inorganic absorbent systems using molecular sieves and zeolite 13X were also applied to synthesis of cyclic carbonates like ethylene carbonate, propylene carbonate and glycerol carbonate (Table 2 entries 19-22).[26e,f] In particular, the combination of zeolite 13X raised the yield of cyclic carbonates and the yields were 35-61% with high selectivity at 393 K (Table 2 entry 20-22). It has been confirmed that this system can be applied to various organic carbonate synthesis without loss of selectivity.

3.2 Reactive dehydration system

Reactive dehydration system means that dehydration of the reaction mixture is performed by using dehydration reagents such as inorganic or organic compounds that can react with water. Reactive dehydration system can be classified into two types: non-catalytic dehydration system and catalytic dehydration system, which means dehydration without catalysts and dehydration with catalysts, respectively. The reaction system with dehydration reagents has the advantage that dehydration reagents can work even at far above 373 K, which is different from the case of inorganic absorbents. In addition, the energy change derived from hydration of dehydration reagent (nitrile: ΔH = ~-90 kJ/mol) is much higher than that in the case of DMC synthesis (Figure 2), therefore, the energy can be used as a driving force for the DMC synthesis as a heat. On the other hand, the choice of a suitable dehydrating agent is important from the following three aspects. One aspect is that the direct synthesis of DMC will turn to be unattractive if more toxic and/or corrosive reactants than phosgene or CO are used as a reactant of hydration. The second is that the formation of by-products derived from dehydration reagents may bring the waste or the difficulty of separation from DMC. The third is that acidity or basicity of dehydration reagents and the products by hydration may cause some side reactions or catalyst deactivation. Therefore, the dehydration reagents should be neutral, safe and easy to handle, and it is desirable that the products by hydration are valuable and useful chemicals or can be easily recycled.

3.2.1 Non-catalytic hydration system

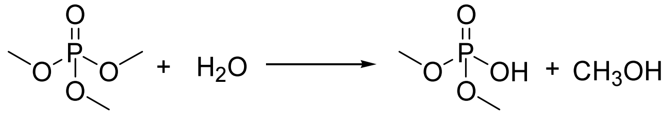
The dehydration reagents that can be used in non-catalytic hydration system must be highly reactive with water at the moderate conditions. Versatile dehydration reagents have been employed such as CH_3I, trimethyl phosphate (TMP), dicyclohexyl carbodiimide (DCC), acetals, butylene oxide and ionic liquid. The summarized data are shown in Table 3.

3.2.1.1 CH_3I

CH_3I has been used as a promoting reagent for DMC formation from CO_2 and methanol although CH_3I is a little toxic and difficult to handle due to the low boiling point. Fujimoto and co-workers first applied CH_3I to the DMC synthesis with K_2CO_3 catalyst, providing 12.3% yield of DMC at 373 K in 2h (Table 3 entry 1).[27a] In addition, Arai and co-workers and Liu and co-workers also demonstrated that CH_3I and CH_3I + molecular sieves 4A improve DMC yield and methanol conversion, respectively (Table 3 entries 2 and 3).[27b,c] The obtained yields were much higher than the equilibrium one, which indicates that addition of CH_3I shifts the chemical equilibrium to the DMC formation side. The reaction mechanism by K_2CO_3 combined with CH_3I was proposed as follows (Scheme 2); (I) activation of methanol by a base. (II) CO_2 insertion to the produced methoxide. (III) DMC formation through methylation by CH_3I. (IV) formation of HI and (V) regeneration of CH_3I by the reaction of HI and methanol. Taking this reaction mechanism into consideration, two reasons for improvement of DMC yield by CH_3I can be considered. One is that Eq (V) in Scheme 2 is an equilibrium reaction and the reaction of CH_3I with H_2O can reduce the content of water in the reaction system. The other one is the reaction of K_2CO_3 with two molar of HI to afford one molar of H_2O (Scheme 2 (VI))[27], in that one molar of HI produces one half molar of H_2O, which is less than that of the normal reaction mechanism where one molar of HI produces one molar of H_2O (Scheme 2 (V)). This means that the side reaction (VI) reduced the produced water with respect to HI amount. Therefore, CH_3I will directly or indirectly work as a dehydration reagent.

3.2.1.2 Trimethylphosphate (TMP)

Trimethylphosphate (TMP) is known to be a mild scavenger of H_2O under the neutral conditions. Kizlink reported that combination of TMP with $Bu_2Sn(OBu)_2$ catalyst and $Ti(OBu)_4$ catalyst raised the DMC yield to 4.7 and 2.9%, respectively, which are higher than the equilibrium one (Table 3 entries 4 and 5).[18b,f] Therefore, effectiveness of the system with TMP was confirmed in DMC synthesis. The dehydration reaction by TMP is shown below (Eq. 2).

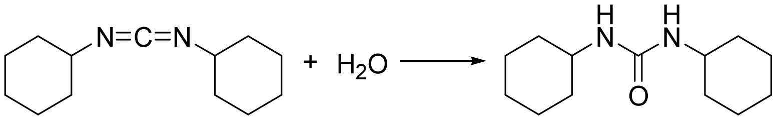


(Eq. 2)

TMP can react with H_2O even at 353 K without a catalyst to afford dimethyl phosphate and methanol.[28] However, this method is not preferable from the viewpoints of corrosion behavior of phosphoric acid, wastes from TMP and low yield of DMC.

3.2.1.3 Dicyclohexyl carbodiimide (DCC)

Dicyclohexyl carbodiimide (DCC) is often used for dehydration in the fields of organic and synthetic chemistry. The hydration of DCC is described in Eq. 3 and dicyclohexyl urea is formed.



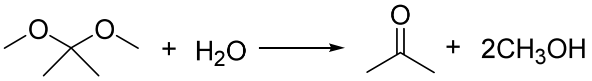
(3)

However, this dehydration system has drawbacks such as difficulty of removal of produced dicyclohexyl urea and nature of allergen of DCC.[30] DMC yields were improved to 6.7% and 4.0% by addition of DCC in the presence of $Bu_2Sn(OBu)_2$ (Table 3 entry 6) and $Ti(OBu)_4$ catalyst (Table 3 entry 7), respectively.[18b,f] And also, Aresta and co-workers reported that DCC is effective not only as a dehydrating reagent but also as a promoter by activation of methanol when CuCl is used as a catalyst.[29] This catalyst system showed excellent DMC yield based on the dehydration reagent (93%), however, DMC yield based on methanol is very low (1.7%). The DMC yield based on methanol should be high because the residual methanol is difficult to be removed due to the azeotrope nature of methanol and DMC. On the other hand, this catalyst system can be introduced into ethanol and ally alcohol to afford diethylcarbonate (DEC) and diallylcarbonate in 1.3% and 12% yield, respectively (Table 3 entries 9 and 10).

Fortunately, DCC can be regenerated from co-produced urea in the presence of $NbCl_5$.[31] Therefore, DCC system will be promising if high organic carbonate yield based on methanol can be obtained with stoichiometric amount of DCC.

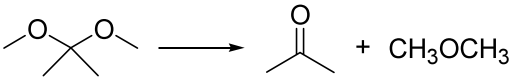
3.2.1.4 Acetals

Acetals are frequently adopted as a dehydration reagent in organic synthesis since acetals are inexpensive and easily generated from ketones. Both the reactions of direct DMC formation from methanol and CO_2 and the hydration of 2,2-dimethoxypropane (DMP) (Eq. 4) proceeded in the presence of $Bu_2Sn(OMe)_2$ at the same time, and the obtained DMC yields are higher than the equilibrium one with almost the stoichiometric amount of acetone (Table 3 entries 11 and 12).[32a,b,c]



(4)

In addition, the addition of Lewis acidic compounds such as $[Ph_2NH_2]OTf$ or $[C_6F_5NH_3]OTf$ into Bu_2SnO catalyst + DMP reaction system were more effective (Table 3 entries 13 and 14)[32d] since these compounds generally promote the esterification of carboxylic acids. The amount of Lewis acid is crucial for DMC yield, and a very small amount of $[Ph_2NH_2]OTf$ or $[C_6F_5NH_3]OTf$ (0.02 mol% based on methanol) boosts the DMC yield (40% yield of DMC) that is the equilibrium yield in the presence of acetal. DMP was also applied to $Ti(OiPr)_4$ catalyst system where decyl-18-crown-6 is used as a ligand (Table 3 entry 15).[32e] Furthermore, the combination system composed of acetal and a solid catalyst is promising from the viewpoint of reusability of the catalyst. Our group reported that solid CeO_2-ZrO_2 catalyst with DMP can be successfully applied to DMC synthesis to provide high DMC yield (7.2%) (Table 3 entry 16).[32f] In the presence of CeO_2-ZrO_2 solid solutions (Ce/(Ce+Zr)=0.2), DMC formation was saturated at 0.8% without DMP, and dimethyl ether was not detected.[33] The DMC formation rate was increased with addition of DMP. However, the yield showed the volcano trend with respect to the amount of DMP, and the maximum DMC yield reached 7%. In the larger amount of DMP, the amount of the produced acetone is larger than that of DMC amount, and the yield of dimethyl ether also increased. These results imply that acetone is produced not only by the hydration of acetal but also by the degradation of acetal (Eq. 5). Therefore, the decrease of the activity and DMC yield in a larger amount of DMP can be explained by the unfavorable equilibrium of Eq 4, which is caused by a large amount of acetone produced by decomposition of DMP (Eq. 5).

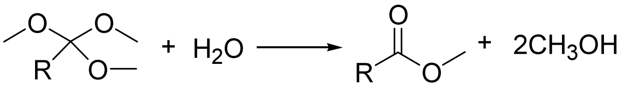


(5)

On the other hand, combination system of 4-methyl-2,2-pentamethylene-1,3-dioxolane and $Bu_2Sn(OMe)_2$ was applied to the synthesis of propylene carbonate, giving 3.4% yield of the product. As above, although the control of side reactions of acetal is required owing to the high reactivity of acetal, acetal is an effective dehydration reagent which can co-work with various homogeneous and heterogeneous catalysts.

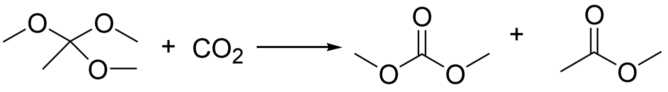
3.2.1.5 Ortho ester

Ortho ester is also used as a dehydration reagent because it can be subject to addition of water as shown in Eq. 6.



(6)

Liu and co-workers reported combination of 1,1,1-trimethoxymethane (TMM) with [Emim]/$Ce_{0.5}Zr_{0.5}O_2$ ([Emim]=1-ethyl-3-methyl imidazolium) is effective for DMC formation reaction, and the obtained yield is 10% (Table 3 entry 18).[34] This result is superior to that of the system without dehydration reagents, indicating that hydration of TMM proceeded absolutely. In contrast, Sakakura et al. investigated the reaction of 1,1,1-trimethoxyethane and CO_2 using $Bu_2Sn(OMe)_2$ catalyst in the absence of methanol.[35]



(7)

Although Eq. 7 is thermodynamically favorable, ortho esters are expensive and not suitable as a starting material for industrial use. In addition, the regeneration of ortho esters from esters and alcohols is not easy.

3.2.1.6 Butylene oxide

Murzin et al. investigated dehydration effect of butylene oxide in DMC formation reaction (Table 3 entries 19 and 20).[36a,b] The initial reaction rate of butylene oxide with water (≥ 0.06 s^{-1}) is higher than those of ortho esters and acetals under the same reaction conditions (≤ 0.01 s^{-1}), which suggests that butylene oxide is highly reactive. In DMC formation reaction, the reaction scheme is a little complicated due to the high reactivity of butylene oxide as shown in Scheme 3. DMC synthesis from methanol and CO_2 and reaction of butylene oxide with the produced water to 1,2-butanediol are desirable reactions, however, side reactions such as the reaction of butylene oxide with methanol and CO_2 are inevitable, leading to decrease of the DMC selectivity and efficiency of the dehydration reagent. DMC yields in the absence and presence of butylene oxide over ZrO_2-KCl-MgO catalyst was 0.2% and 7.2%[36a], respectively. Hence, the addition of butylene oxide is effective for DMC synthesis. However, the above side reactions reduced the DMC selectivity (<10.0-63.4%). In addition, in this reaction system, about half of butylene oxide was used for the side reaction of butylene oxide and CO_2. The kinetic study revealed that the reaction rate of butylene oxide with water is at most twice as large as that with methanol. It has been also reported the combination of butylene oxide with CeO_2 catalyst is effective for DEC synthesis from CO_2 and ethanol (Table 3 entry 21).[36c,d]

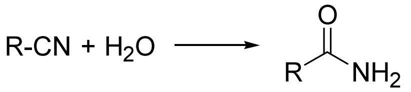
3.2.1.7 Ionic liquids

Recently, ionic liquids have been adopted as a promoter and/or activator of CO_2 to DMC synthesis from CO_2 and methanol.[37] The methoxide ionic liquid supported ZrO_2-MgO ([Bmim][MeO]/ZrO_2-MgO; [Bmim]=1-butyl-3-methylimidazolium chloride) improved the DMC yield up to 12.7% (Table 3 entry 22).[37a] This can be because MeO^- in the ionic liquid is substituted for OH^- of the produced water (anion exchange), leading to decrease of water in the reaction media. The catalyst can be regenerated and reused by treatment of sodium methoxide in methanol solution after the reaction. In addition, $H_3PW_{12}O_{40}/Ce_{0.1}Ti_{0.9}O_2$ with an ionic liquid of [Emin]Cl also showed high DMC yield 13.0%, which is higher than $H_3PW_{12}O_{40}/Ce_{0.1}Ti_{0.9}O_2$ catalyst alone (6.0%) (Table 3 entry 23).[37b] A kind of the counter anion of imidazolium ion affected the DMC yield, which suggests that the counter anion will play an important role for removal of water. From these results, the ionic liquid will work as an effective dehydration reagent through the anion exchange mechanism. Furthermore, combination dehydration system of CH_3I + [Bmim]Cl using K_2CO_3 catalyst and microwave irradiation at low temperature is also effective for DMC synthesis (Table 3 entry 24) to give 14% yield of DMC.[37c] From the calculation of the absorption state of CO_2 on ionic liquid by DFT, the authors also stated that the role of ionic liquid is interaction of CO_2, which is attributed to the acceleration of the reaction.

3.2.2 Catalytic hydration system

Various dehydration systems were presented as above such as gas phase reaction system, membrane separation system, inorganic absorbent system and non-catalytic hydration system. These systems are effective and certainly increased the DMC yield to some extent. In particular, combination of reactive hydration reagents showed good results in comparison with the other systems except for the system of a molecular sieve 3A with $Bu_2Sn(OMe)_2$ catalyst (Table 2 entry 17). These results mean that combination of reactive hydration reagents is promising for DMC synthesis. However, the yields of DMC by non-catalytic dehydration reagents are below 40%, which can be explained by the high reactivity of the dehydration reagents and the chemical equilibrium of the dehydration reagents. The dehydration reagents such as butylene oxide or CH_3I as mentioned above are highly reactive with water at ambient temperature without catalyst, leading to deactivation of catalysts and the decrease of DMC yield and the dehydration reagent amount by side reactions. To overcome these drawbacks, one attractive method is catalyzed reactive dehydration system, which means that dehydration reagents are hydrated by catalysts, which leads to removal of water from the reaction media. In particular, the dehydration reagents should be hydrated only by a catalyst. This system is expected to bring about high selectivity due to low reactivity of the dehydration reagents and shift the chemical equilibrium to the product side by hydration reaction. However, selection of catalyst, catalytic hydration reaction and dehydration reagents is quite difficult because both DMC formation reaction and hydration reaction of dehydration reagents are simultaneously catalyzed by only a catalyst or combined catalysts under the same reaction conditions. As mentioned above, our group studied DMC synthesis from CO_2 and methanol, and found that CeO_2 is effective for activation of CO_2 and methanol due to its acid-base property.[14b, 19f, 20a,i, 30f, 31a,b, 38] Envisioning that catalytic hydration reaction combined with CeO_2 will lead to great achievement in DMC synthesis, we investigated suitable catalytic hydration reaction by CeO_2 and found that CeO_2 can catalyze DMC formation reaction and hydration of nitriles at the same time under the same reaction conditions (Table 3 entries 1-3, 15-19 and 22) (Scheme 4).[38a-d] The detailed results are shown below.

First, acetonitrile hydration was used as a catalytic hydration reaction.[38a,b] DMC yield was obtained in 8.9% at low CO_2 pressure of 0.5 MPa, which is much higher than the equilibrium yield (0.08%) (Table 4 entry 1). However, the selectivity of DMC is 65% because of fomation of methylcarbamate and methylacetate. These by-products are formed by the following reactions; nitrile hydration produced amide (Eq. 8). A part of amide reacted with methanol to give ester and NH_3 (Eq. 9). In addition, DMC and the produced NH_3 can be transformed to methyl carbamate (Eq. 10).



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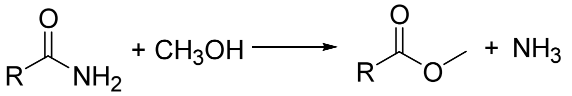

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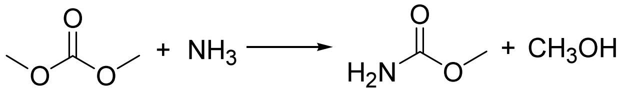
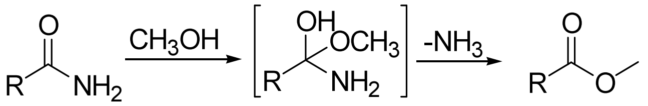


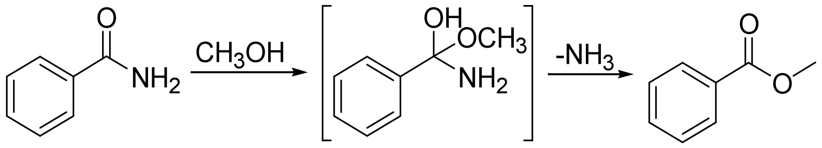
(10)

Surprisingly, the DMC formation rate in combination with acetonitrile hydration was decreased as CO_2 pressure was increased (Figure 3), which is opposite tendency to that of the previous reports regarding DMC synthesis without nitriles.[15, 24d, 26b] To clarify the cause, effect of CO_2 pressure on acetonitrile hydration was investigated by adding a small amount of water (Figure 4). On adding water in the reaction media, only acetamide and methyl acetate were detected and DMC was not detected because of an equilibrium limitation. The amount of acetamide and methyl acetate was decreased with increasing CO_2 pressure, which is in good accordance with the tendency as shown in Figure 3. These results imply that CO_2 inhibits hydration of acetonitrile, resulting in low yield of DMC at higher CO_2 pressure owing to increase of water content in the reaction media. Therefore, low CO_2 pressure in this reaction system is preferable for acceleration of the reaction. However, there is a serious problem at low CO_2 pressure: At low CO_2 pressure, the amount of methyl acetate was increased by the reaction of Eq. 9, and the reaction of the produced NH_3 with DMC (Eq. 10) results in decrease of DMC yield. Therefore, achieving of high DMC selectivity is not easy. On the other hand, the reaction of ethanol and 1-propanol with CO_2 by the same system of acetonitrile and CeO_2 provided the corresponding cyclic carbonates in high selectivity (94-96%) with similar yields (Table 4 entries 2 and 3), which indicates that the longer chain alcohols can be converted to the corresponding carbonates in higher selectivity. The same strategy with different catalysts like $Zn(OAc)_2$, base catalysts, KI/ZnO and $La_2O_3CO_3$-ZnO was employed to various cyclic carbonate syntheses from CO_2 and the corresponding alcohols, providing the moderate yield (7-26%) (Table 4 entries 4-14).[39] However, the selectivities were totally very low (≤64%) except for the case of Cs_2CO_3 catalyst.

In order to obtain high DMC yield and selectivity, the over-reactions of the produced amide or nitrile must be suppressed. Benzamide is expected to be more stable than acetamide because of the resonance between amide and phenyl ring. Considering that the reaction of amide with methanol proceeds via the iminoalcohol intermediate (Eq. 11), the resonance between the amide group and phenyl ring will be broken when benzamide turns into the iminoalcohol intermediate (Eq. 12), which will produce high energy barrier. In contrast, in the case of acetonitrile, lower energy barrier between acetamide and the iminoalcohol intermediate can be expected because there is no resonance in the reaction of acetamide.



(11)

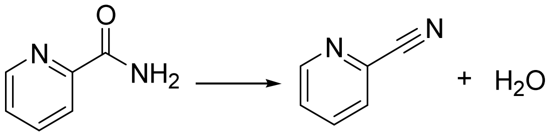


(12)

Then, hydration of benzonitrile was applied to CeO_2-catalyzed DMC formation reaction (Table 4 entry 15).[38c] As expected, the selectivity of benzamide (78%) is higher than that of acetamide. The effect of CO_2 pressure in the presence of benzonitrile hydration was investigated. DMC formation rate was increased with decreasing the CO_2 pressure, which is similar tendency to the result of acetonitrile hydration. The DMC yield reached 47% in 86 h under 1 MPa of CO_2 pressure. This value is comparable to the reaction system using the circulation system between the reactor and molecular sieve (Table 2 entry 17).[26b,c] However, the DMC yield was not improved in further reaction time although a large amount of methanol, CO_2 and benzonitrile still remained in the autoclave reactor. In order to investigate the effect of benzamide, benzamide was added to the reaction of $CH_3OH + CO_2 + C_6H_5CN$ (Figure 5), which causes deactivation of CeO_2. Addition of benzamide decreased the DMC formation rate significantly, even if the added amount of benzamide was 2 mmol (200 mol% based on CeO_2). In particular, the addition of 10 mmol (1000 mol% based on CeO_2) of benzamide completely prevented the DMC formation under these reaction conditions. In addition, FTIR analysis revealed that benzamide is adsorbed on CeO_2 after reaction. These results suggest that benzamide causes the catalyst poisoning, which is also supported by the result of TG-DTA analysis of used CeO_2. The strong adsorption of benzamide will be derived from the extraction of proton in the amide group by the base site of CeO_2 (Scheme 5). The calcination treatment of used CeO_2 can regenerate the active CeO_2 by removal of adsorbed benzamide, providing the same activity without loss of selectivity. This catalyst system was applied to other alcohols such as 1-propanol, 2-propanol and benzylalcohol (Table 4 entries 15-19). Compared with DMC synthesis by this system, the yields from other alcohols were much lower, although the reactivities of these alcohols are almost the same as that of methanol except for benzylalcohol. The same dehydration reagent with K_2CO_3 catalyst was used for cyclic carbonate syntheses from 1,2-propanediol and octane-1,2-diol, affording the products in moderate yields (10-20%) with low selectivity (45%) (Table 4 entries 20 and 21).[40] The yield and selectivity in the benzonitrile dehydration system were improved in comparison with the acetonitrile dehydration system, but are far from the satisfactory level of yield.

In order to realize the higher DMC yield, deactivation of CeO_2 by adsorption of amide should be removed. The recent study reported that CeO_2 shows the substrate specificity for nitriles that have a heteroatom (N or O) adjacent to the α-carbon atom of the CN group although the reaction conditions are very different from the DMC synthesis: solvent is water and reaction temperature is

303 K.[41] We chose 2-cyanopyridine instead of benzonitrile and examined the effect of 2-cyanopyridine in DMC synthesis (Table 4 entry 22).[38d] The time course of the reaction is shown in Figure 6. Methanol and 2-cyanopyridine were consumed in a ratio of 2:1, and equimolar amounts of DMC and 2-picolinamide were formed according to the reaction stoichiometry with increasing reaction time. The methanol-based yield of DMC and 2-cyanopyridine-based yield of 2-picolinamide were 94 and 95% at 12 h, respectively. Almost complete conversion of methanol to DMC using CO_2 as a carbonyl source was achieved for the first time. In addition, nitriles with a cyano group at a 2-position of pyridine ring have a drastic effect on DMC yield, for example, 2-cyanopyridine, pyrazine-2-carbonitrile and 2-cyanopyrimidine produced DMC with 94%, 91% and 39%, respectively (Table 5 entries 1-3). In contrast, 3- and 4-cyanopyridines gave only 2.1% and 4.1% of DMC, respectively, and the nitriles without pyridine ring were not effective in the condition where only stoichiometric amount of nitrile was used (Table 5 entries 4-9). 2-Cyanopyridine has two important roles: one is the high ability of hydration and the second is desorption of the produced 2-picolinamide from CeO_2 surface. This is probably because 2-picolinamide forms intermolecular hydrogen-bonds between the H atoms in the amide groups and the N atoms of the pyridine rings neighboring the amide groups, and weakens the interaction between the NH_2 groups and the base site of CeO_2 on the catalyst surface to suppress the poisoning of CeO_2 (Scheme 5). In actual, the addition of a large amount of 2-picolinamide (50 mmol) did not bring any effect on DMC formation rate and yield. On the other hand, it is also important to regenerate 2-cyanopyridine from 2-picolinamide. We found that the produced 2-picolinamide can be easily separated from the reaction mixture. Figure 7 shows the flow chart for separation of 2-picolinamide (unpublished data). 2-Picolinamide is in the solid state at room temperature, and the solid materials including 2-picolinamide and CeO_2 can be separated from the other compounds by addition of *n*-hexane because 2-picolinamide is insoluble in hexane and the other organic compounds are soluble in hexane. On the other hand, 2-picolinamide can be dissolved in acetone, which enables separation of 2-picolinamide from CeO_2 by filtration. Evaporating acetone, the 2-picolinamide can be obtained in 97% recovery percentage with >99% purity. In addition, we prepared for Na_2O/SiO_2 catalyst for the dehydration of 2-picolinamide to 2-cyanopyridine (Eq. 12) using a Soxhlet reactor.



(12)

Although a long reaction time is needed at present, the yield of 2-cyanopyridine is 84% with >99% selectivity.[38d] Therefore, the recycling system of 2-picolinamide was established with a room for improvement. As above, catalytically reactive hydration system using CeO_2 and 2-cyanopyridine first enables the direct synthesis of DMC from methanol and CO_2 in almost quantitative yield. In this system, carboxylation of methanol and hydration of nitriles simultaneously and effectively proceeded over CeO_2, which leads to high yield. The acid-base bifunctional property of CeO_2 will function as an effective catalyst for both the reactions. This unique property of CeO_2 is also successfully applied to various organic syntheses in liquid phase.[42] This catalyst system composed of CeO_2 and 2-cyanopyridine will be expected to expand to various carbonates synthesis including cyclic carbonates or liner carbonates. However, the drawback of this reaction system is dehydration of amide. In the future, new system for recycle of hydration reagents is desired to be explored. Moreover, development of new catalytic hydration systems is also expected.

4. Conclusions and outlook

Recent advances of direct organic carbonates synthesis from CO_2 and alcohols have been summarized particularly focusing on the dehydration systems. The dehydration system is necessary for direct organic carbonate synthesis for achieving high yield owing to the limitation of chemical equilibrium. Various effective dehydration systems such as non-reactive dehydration system and reactive dehydration system have been developed up to date, where non-reactive hydration system includes gas-phase system, membrane separation system and inorganic absorbent system, and reactive hydration system includes non-catalytic hydration system using reactive hydration reagents like CH_3I, TMP, DCC, acetal, ortho ester, butylene oxide and catalytic hydration system using the hydration reagent that can be hydrated only by catalysts. Among these dehydration systems, the reactive hydration system, in particular, catalytic hydration system with nitriles is the most efficient for organic carbonate synthesis. Especially, combination of 2-cyanopyridine with CeO_2 achieved high DMC yield of 94% with 96% selectivity. Although the selection of catalyst and dehydration reaction and reagent is difficult because these factors must work simultaneously under the same reactions, in the future, it is expected that development of the new dehydration systems is accelerated.

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Table 1 DMC synthesis from methanol + CO_2 without dehydration systems[a]

Entry	Catalyst	P_{CO2} / MPa	T / K	t / h	Yield / %	Selc. / %	Ref.
Homogeneous catalyst system							
1	$Bu_2Sn(OBu)_2 + I_2$	2.8	453	20	4.4	-	18a,b
2	$CH_3OK + CH_3I$	7.3	353	10	0.02	>99	18c,d
3	Tl(OEt)	0.3	423	70	0.3	-	18e
4	$Ti(OBu)_4$	2.5	453	20	2.8	-	18f
5	$Ni(OAc)_2 \cdot 4H_2O$	7	413	12	2.1	>99	18g
6	$[Nb(OMe)_5]_2$	5	423	28	1.8	-	18h
7	Mg	15	453	12	1.2	>99	18i
Heterogeneous catalyst system							
8	ZrO_2	6	433	16	1.0	>99	19a,b
9	ZrO_2/SiO_2	20	423	130	0.4	-	19c
10	ZrO_2/C	0.1	353	1	0.47	-	19d
11	H_3PO_4/ZrO_2	6	403	2	0.3	>99	19e,f
12	$H_3PW_{12}O_{40}/ZrO_2$	(175 mmol)	373	7	4.3	>99	19g
14	CeO_2-ZrO_2	6	383	16	1.7	>99	20a
15	$Ce_{0.5}Zr_{0.5}O_2$	20	373	24	1.4	-	20b
16	$Ce_{0.8}Zr_{0.2}O_2$	5	443	1	0.7	-	20c
17	$Ga_2O_3/Ce_{0.6}Zr_{0.4}O_2$	6	443	3	0.45	>99	20d,e,f
18	$H_3PW_{12}O_{40}/Ce_{0.6}Zr_{0.4}O_2$	6	443	3	0.25	>99	20g
19	$Ce_{0.5}Zr_{0.4}Y_{0.1}O_2$	20	373	24	0.8	-	20h
20	CeO_2	6	403	4	0.7	>99	20i
21	CeO_2	5	413	2	0.43	-	20j
22	$H_3PW_{12}O_{40}/Ce_{0.1}Ti_{0.9}O_2$	5	443	12	5	>99	20k,l,m
23	Al_2O_3/CeO_2	5	408	5	2.1	>99	20n,o
24	$Cu_{1.5}PMo_{12}O_{40}$	0.12	323	1	1.7	28	21
25	SnO_2	20	423	100	1.6	9	22a
26	Sn/SBA-15	18	513	10	0.07	-	22b
27	Sn/SBA-15	18	473	190	0.08	-	22c
28	Sn-SBA-CH_3	20	423	70	0.65	>99	22d
29	Sn-Ph-PMOs-4.0	18	453	30	0.01	-	22e
30	$Co_{1.5}PW_{12}O_{40}$	0.5	353	5	2.4	65	22f,g
31	Rh/ZSM-5	0.1	393	-	0.2	42	23a
32	Polystylene-Nb	11.4	408	15	1.9	-	23b

[a]- means no data.

Table 2 Non-reactive dehydration systems for organic carbonate synthesis from CO_2 and alcohol[a]

Entry	Catalyst	Dehydrating agent	Alcohol	P_{CO2} / MPa	T / K	t / h	Yield / %	Selc. / %	Ref.
Gas phase reaction system									
1	Cu-Ni/VSO	-	MeOH	0.6	453	-	4.5	58	24a
2	Cu-Ni/VO + Photo irradiation (UV)	-	MeOH	1.2	393	-	4.0	85	24b
3	Cu-Ni-V/AC (Active carbon)	-	MeOH	1.2	383	3	7.0	90	24c
4	Cu-Ni/Graphite	-	MeOH	1.2	378	-	9.0	88	24d
5	Cu-Ni/Graphite oxide	-	MeOH	1.2	378	3	9.1	90	24e
6	Cu-Ni/TEG (Thermally expanded graphite)	-	MeOH	1.2	373	-	4.4	89	24f
7	Cu-Ni/MWCNTs (Multi-walled carbon nanotubes)	-	MeOH	1.2	393	-	3.7	85	24g
8	$CuCl_2$/AC (Active carbon)	-	MeOH	1.2	393	4	(4.8 mmol h^{-1})	90	24h
9	Cu-Ni/GNS (Graphene nanosheet)	-	MeOH	1.2	393	3	7.6	83	24i
10	Cu-Ni/Diatomite	-	MeOH	1.2	393	GHSV = 600 h^{-1}	4.1	91	24j
11	Cu-Fe/SiO_2	-	MeOH	1.2	393	SV = 360 h^{-1}	4.6	86	24k
12	Cu-Fe-Mo/SiO_2	-	MeOH	0.6	393	SV = 360 h^{-1}	6.1	88	24l
13	$Co_{1.5}PW_{12}O_{40}$	-	MeOH	(60 ml/min.)	473	MWHSV = 3.25 h^{-1}	6.6	87	24m,n
Membrane separation system									
14	Cu-KF/MgSiO	Polyimide-silica hybrid membrane	MeOH	0.4	403	SV = 1480 h^{-1}	8.8	96	25a
15	Nb_2O_5/CeO_2	NaA-type tubular ceramic membrane	EtOH	30	408	-	2.3	>99	25b
Inorganic absorbent system									
16	ZrPP-HF	Molecular sieve 3A	MeOH	4	443	12	1.7	5.3	26a
17	$Bu_2Sn(OMe)_2$	Molecular sieve 3A	MeOH	30	453	72	45	-	26b,c
18	Hydrotalcite	Silica lyogel (gas phase reaction)	MeOH	(CH_3OH/CO_2 = 1/25)	403	(0.047 ml min^{-1})	16	>99	26d
19	$Bu_2Sn(OMe)_2$	Molecular sieves	Glycerol	5	450	14	6.9	>99	26e
20	Bu_2SnO	zeolite 13X	EG	14	393	4	61	>99	26f
21	Bu_2SnO	zeolite 13X	1,2-PrD	14	393	4	42	>99	26f
22	Bu_2SnO	zeolite 13X	Glycerol	14	393	4	35	>99	26f

[a] - means no data.

EG: Ethylene glycol, 1,2-PrD: 1,2-propanediol

Table 3 Non-catalytically reactive hydration system for organic carbonate synthesis from CO_2 and the corresponding alcohols[a]

Entry	Catalyst	Dehydrating agent	Alcohol	P_{CO2} / MPa	T / K	t / h	Yield / %	Selc. / %	Ref.
1	K_2CO_3	CH_3I	MeOH	(200 mmol)	353	2	12.3	93	27a
2	K_2CO_3	CH_3I	MeOH	8	343	4	5.2	82	27b
3	-	CH_3I, molecular sieves 4A	MeOH		353	-	(13.4)[b]	-	27c
4	$Bu_2Sn(OBu)_2 + I_2$	Trimethyl phosphate (TMP)	MeOH	2.8	453	20	4.7	-	18b
5	$Ti(OBu)_4$	Trimethyl phosphate (TMP)	MeOH	2.5	423	20	2.9	-	18f
6	$Bu_2Sn(OBu)_2 + I_2$	Dicyclohexyl carbodiimide (DCC)	MeOH	2.8	453	20	6.7	-	18b
7	$Ti(OBu)_4$	Dicyclohexyl carbodiimide (DCC)	MeOH	2.5	423	20	4.0	-	18f
8	CuCl	Dicyclohexyl carbodiimide (DCC)	MeOH	5	338	24	1.7	-	29
9	CuCl	Dicylcohexyl carbodiimide (DCC)	EtOH	5	338	24	1.3	-	29
10	Cu_2I_2	Dicylcohexyl carbodiimide (DCC)	Allyl alcohol	5	338	4	12	-	29
11	$Bu_2Sn(OMe)_2$	2,2-Dimethoxypropane (DMP)	MeOH	200	453	24	9.4	>99	32a,b
12	$Bu_2Sn(OMe)_2$	2,2-Dimethoxypropane (DMP)	MeOH	20	423	96	1.6	>99	32c
13	$Bu_2SnO + [Ph_2NH_2]OTf$	2,2-Dimethoxypropane (DMP)	MeOH	30	453	24	40	>99	32d
14	$Bu_2SnO + [C_6F_5NH_3]OTf$	2,2-Dimethoxypropane (DMP)	MeOH	30	453	24	40	>99	32d
15	$Ti(O\textit{i}Pr)_4$ + decyl-18-crown-6	2,2-Dimethoxypropane (DMP)	MeOH	30	453	24	5.6	-	32e
16	CeO_2-ZrO_2	2,2-Dimethoxypropane (DMP)	MeOH	(200 mmol)	383	140	7.2	97	32f
17	$Bu_2Sn(OMe)_2$	4-Methyl-2,2-pentamethylene-1,3-dioxolane	1,2-PrD	15	453	12	3.4	-	32g
18	$Ce_{0.5}Zr_{0.5}O_2$	1,1,1-Trimethoxymethane (TMM)	MeOH	12	373	34	10	-	34
19	ZrO_2-KCl-MgO	Butylene oxide	MeOH	5	423	8	7.2	53	36a
20	ZrO_2-MgO	Butylene oxide	MeOH	9	423	8	6.2	53	36b
21	CeO_2	Butylene oxide	EtOH	4.5	453	25	1.6	-	36c,d
22	[Bmim][MeO]/ZrO_2-MgO	([Bmim][MeO])	MeOH	8	393	9	12.7	86	37a
23	$H_3PW_{12}O_{40}/Ce_{0.1}Ti_{0.9}O_2$	EMImCl	MeOH	2.4	413	6	13.0	>99	37b
24	K_2CO_3 (+Microwave irradiation)	CH_3I + [Bmim]Cl	MeOH	0.1	-	0.7	14	-	37c

[a] - means no data.

[b] The number in parenthesis is conversion of methanol.

1,2-PrD: 1,2-propanediol

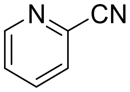
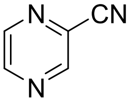
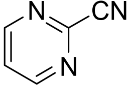
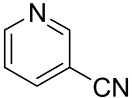
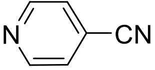
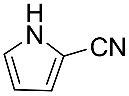
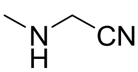
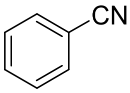
Table 4 Catalytic reactive hydration system for organic carbonate synthesis from CO_2 and alcohol[a]

Entry	Catalyst	Dehydrating agent	Alcohol	P_{CO2} / MPa	T / K	t / h	Yield / %	Selc. / %	Ref.
1	CeO_2	Acetonitrile	MeOH	0.5	423	48	8.9	65	38a,b
2	CeO_2	Acetonitrile	EtOH	0.5	423	16	7.5	94	38b
3	CeO_2	Acetonitrile	1-Propanol	0.2	423	24	5.1	96	38b
4	$Zn(OAc)_2$	Acetonitrile	EG	10	443	12	11	58	39a
5	$Zn(OAc)_2$	Acetonitrile	1,2-PrD	10	443	12	24	62	39a
6	$Zn(OAc)_2$	Acetonitrile	1,3-PrD	10	443	12	14	61	39a
7	$Zn(OAc)_2$	Acetonitrile	1,2-BuD	10	443	12	17	61	39a
8	$Zn(OAc)_2$	Acetonitrile	1,3-BuD	10	443	12	12	62	39a
9	$Zn(OAc)_2$	Acetonitrile	1,2-PrD	3	433	2	12	64	39b
10	TBD + $(NH_4)_2CO_3$	Acetonitrile	1,2-PrD	10	448	15	22	60	39c
11	Cs_2CO_3 + $(NH_4)_2CO_3$	Acetonitrile	1,2-PrD	10	448	15	11	>99	39d
12	K_2CO_3	Acetonitrile	1,2-PrD	2	423	12	13	53	39e
13	KI/ZnO	Acetonitrile	1,2-PrD	10	433	15	26	61	39f
14	$La_2O_3CO_3$-ZnO	Acetonitrile	Glycerol	4	443	12	7	47	39g
15	CeO_2	Benzonitrile	MeOH	1	423	86	47	78	38c
16	CeO_2	Benzonitrile	EtOH	1	423	24	21	-	38c
17	CeO_2	Benzonitrile	1-Propanol	1	423	24	17	-	38c
18	CeO_2	Benzonitrile	2-Propanol	1	423	24	13	-	38c
19	CeO_2	Benzonitrile	Benzyl alcohol	1	423	24	5	-	38c
20	K_2CO_3	Benzonitrile	1,2-PrD	10	448	18	20	45	40
21	K_2CO_3	Benzonitrile	Octane-1,2-diol	10	448	18	10	-	40
22	CeO_2	2-Cyanopyridine	MeOH	5	393	12	94	96	38d

[a]- means no data.

EG: Ethylene glycol, 1,2-PrD: 1,2-Propanediol, 1,3-PrD: 1,3-Propanediol, 1,2-BuD: 1,2-Butanediol, 1,3-BuD: 1,3-Butanediol

Table 5 DMC synthesis from CO_2 and methanol with various nitriles[38d]

Entry	Nitrile	Methanol conversion / %	Nitrile conversion / %	Yield of products / %[a]			
				DMC	Methyl carbamate	Amide	Ester
1		99	88	94.0	0.99	94.6	1.18
2		98	98	91.2[b]	0.18[b]	86.9[b]	0.26[b]
3		59	91	38.6[b]	0.41[b]	44.1[b]	0.69[b]
4		8	5	2.06	n.d.	3.06	<0.1
5		10	7	4.10	n.d.	2.72	0.20
6		8	5	2.94	n.d.	4.74[c]	n.d.
7		7	10	n.d.	n.d.	<0.1	<0.1
8	H_3C-CN	6	6	0.38	<0.1	0.48	<0.1
9		7	5	0.76	<0.1	0.74	<0.1
10	None	1	-	0.32	-	-	-

Reaction conditions: [a] CeO_2 0.34 g, CH_3OH / nitrile / CO_2 = 100 mmol / 50 mmol / 5 MPa, 393 K, 12 h. [b] 373 K. [c] Yield was calculated based on nitrile conversion because 1*H*-pyrrole-2-carboxamide is not commercially available.

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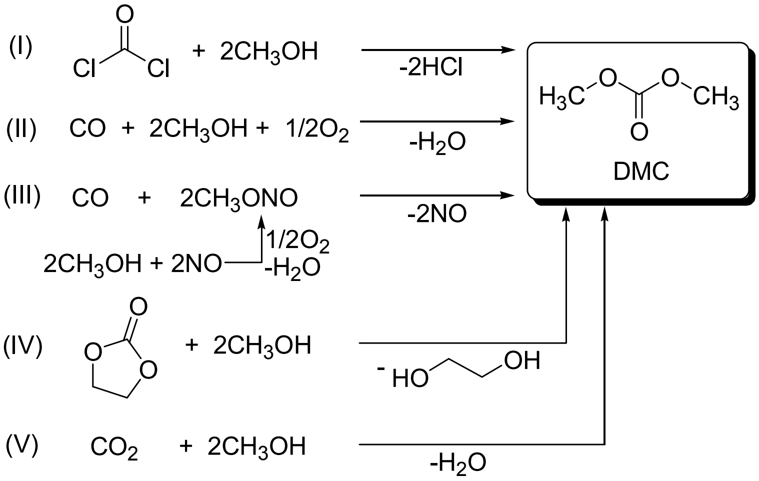
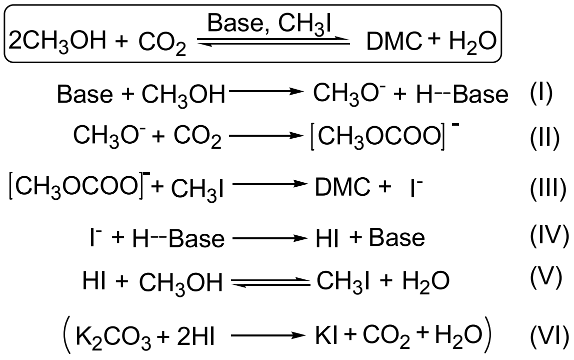
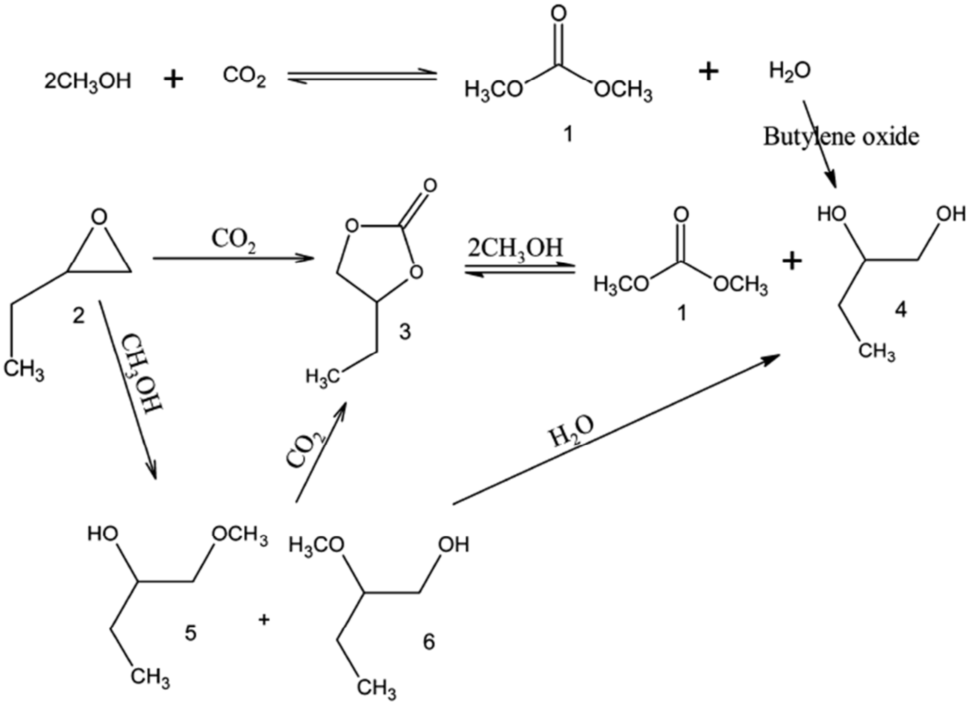


Scheme 1 Synthesis routes of DMC: (I) Phosgene process, (II) Oxidative carbonylation process, (III) two-stage process with CO and NO, (IV) transesterification of cyclic carbonate with methanol and (V) direct synthesis from CO_2 and methanol.

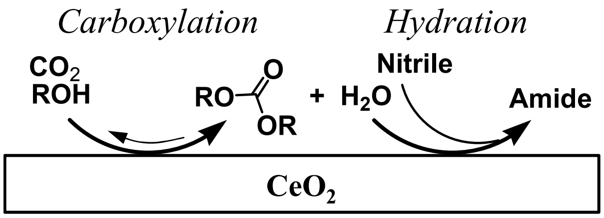


Scheme 2 Proposed reaction mechanism of DMC synthesis from CO_2 and methanol using CH_3I[27a]

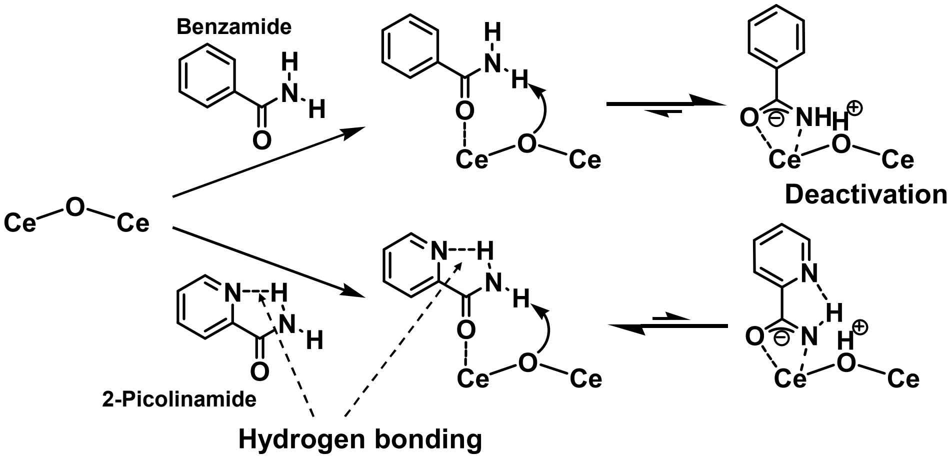


Scheme 3. Formation of DMC and utilization of the co-produced water to form butylene glycol[36a]

Notation: 1, DMC; 2, butylene oxide; 3, butylene carbonate; 4, butylene glycol; 5, 1-methoxy-2-butanol; 6, 2-methoxybutanol. Reprinted with permission from ref. 36a. Copyright (2014) American Chemical Society.



Scheme 4 DMC formation and nitrile hydration over CeO_2



Scheme 5 Adsorption model of benzamide and 2-picolinamide on CeO_2

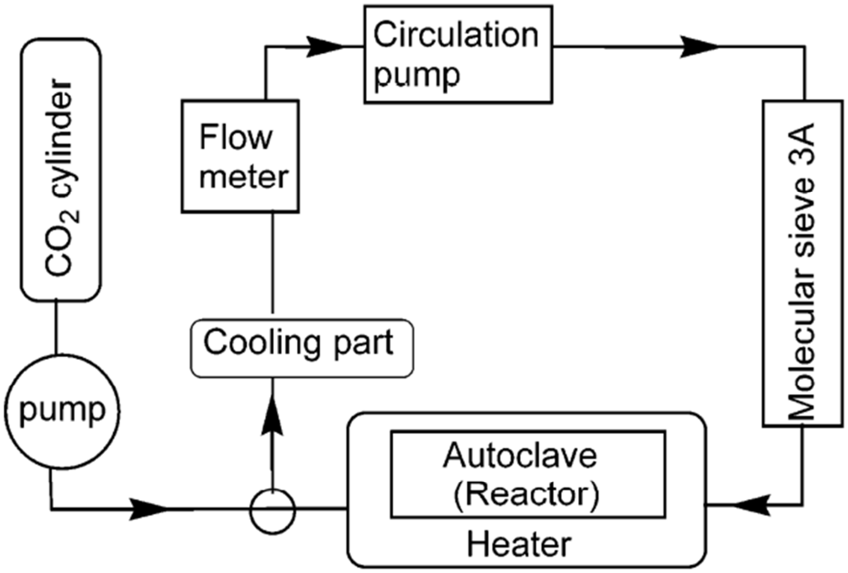


Figure 1 Schematic diagram of a batch reactor with internal recycle[1c]

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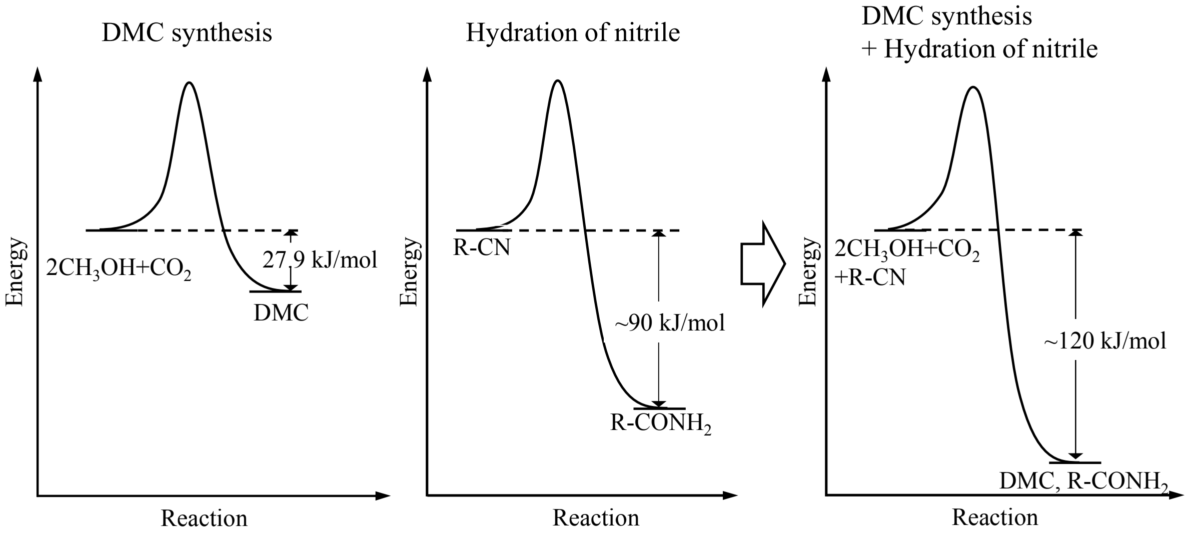

Figure 2 Energy diagram of DMC synthesis, hydration of nitrile and combination system of DMC synthesis + nitrile hydration

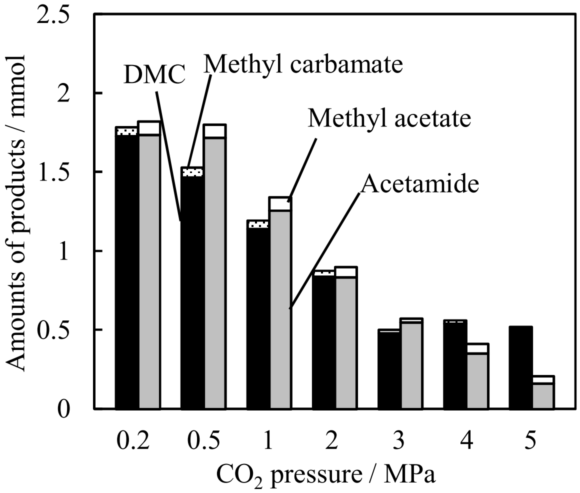

Figure 3 The effect of CO_2 pressure on the amount of products in the reaction of $CH_3OH + CO_2 + CH_3CN$[38b] Reaction conditions: CeO_2 0.17 g, CH_3OH : CH_3CN = 100 mmol : 300 mmol, 423 K, 2 h. Reprinted with permission from ref. 38b. Copyright (2014) Elsevier.

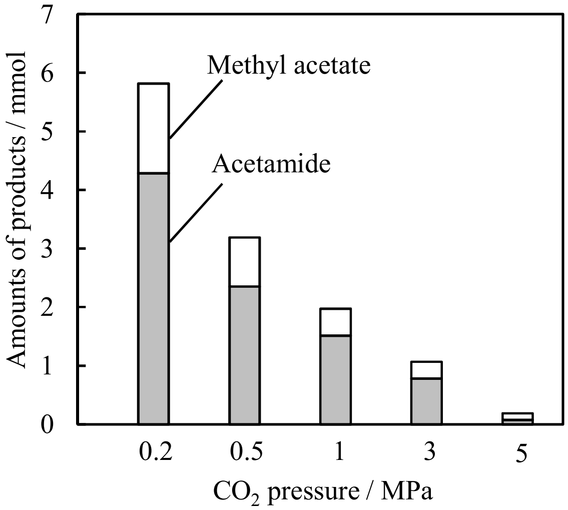

Figure 4 The effect CO_2 pressure on the amount of products in the acetonitrile hydration in the presence of H_2O^{38b}

Reaction conditions: CeO_2 0.17 g, CH_3OH : CH_3CN : H_2O = 100 mmol : 300 mmol : 10 mmol, 423 K, 2 h. Reprinted with permission from ref. 38b. Copyright (2014) Elsevier.

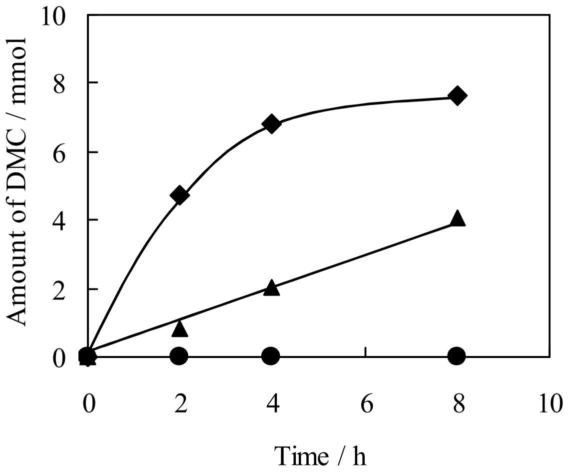

Figure 5 Effect of the addition of $C_6H_5CONH_2$ to the CH_3OH + CO_2 + C_6H_5CN reaction over CeO_2 on the DMC amount[38c]

Reaction conditions: CeO_2 0.17 g, CH_3OH : C_6H_5CN = 100 mmol : 200 mmol, CO_2 1 MPa, reaction temperature 423 K. Amount of added benzamide, ◆: 0 mmol, ▲: 2 mmol, ●: 10 mmol. Reprinted with permission from ref. 38c. Copyright (2014) Wiley.

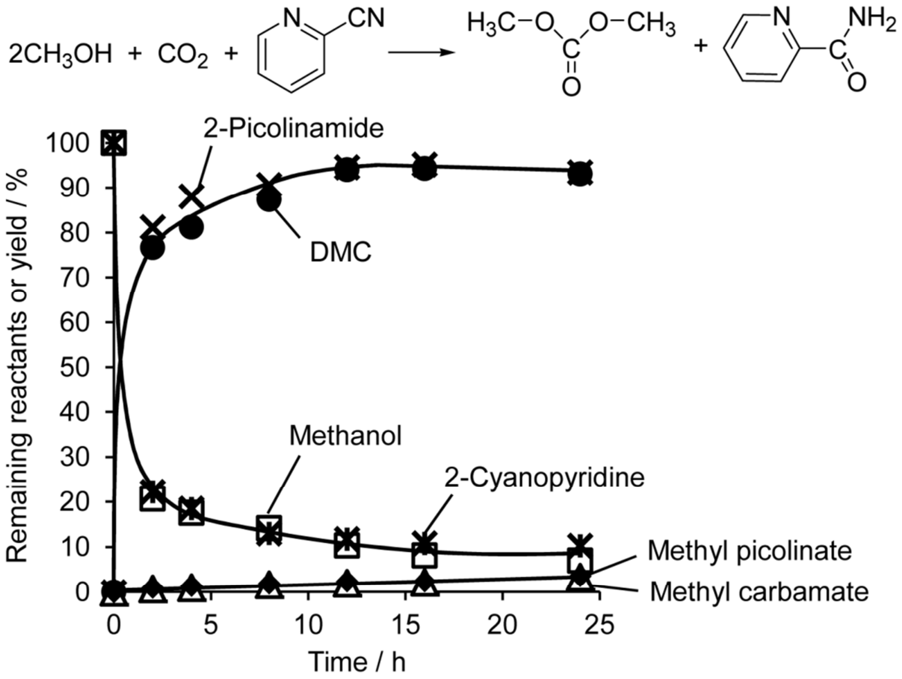

Figure 6 Time course of products of the reaction of $CH_3OH + CO_2$ + 2-cyanopyridine[38d]

Reaction conditions: CeO_2 0.34 g, CH_3OH : 2-cyanopyridine = 100 mmol : 50 mmol, CO_2 5 MPa, 393 K. Reprinted with permission from ref. 38d. Copyright (2014) Wiley.

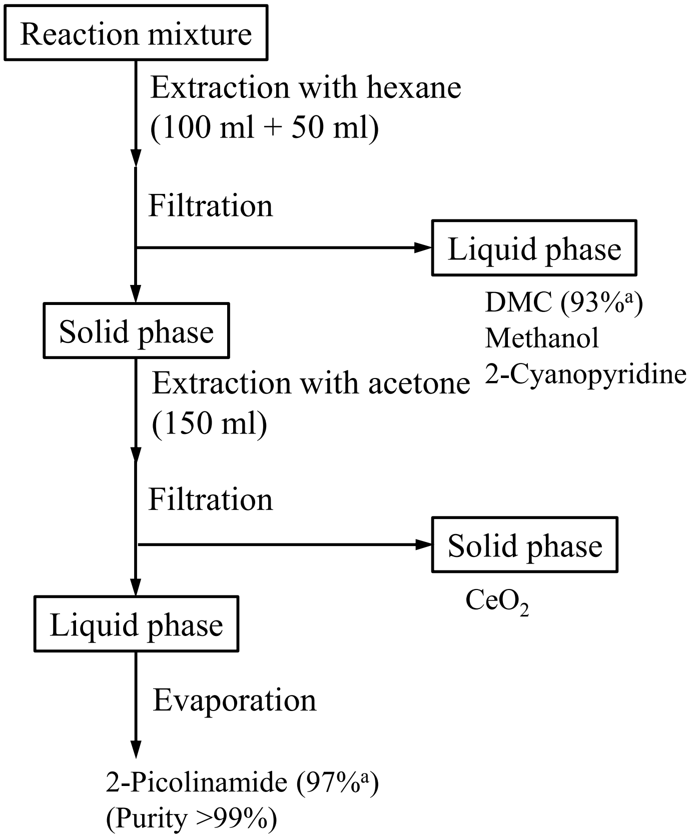

Figure 7 Separation method of 2-picolinamide from the reaction mixture

[a] number in parenthesis is recovery percentage.

Conditions: The reaction mixture contains DMC (86.7 mmol), CH_3OH (30 mmol), methyl carbamate (1.6 mmol), 2-cyanopyridine (10.3 mmol), 2-picolinamide (87.5 mmol), methyl picolinate (2.2 mmol) and CeO_2 (0.17 g). Extraction of the reaction mixture was performed two times with hexane (100 ml (first time) and 50 ml (second time)), and extraction of solid phase was performed with 150 ml acetone.